Exploratory Studies of Novel Sodium-ion Battery Systems

Xiao-Qing Yang and Enyuan Hu
Brookhaven National Lab. (BNL)

2020 DOE Vehicle Technologies Office
Annual Merit Review

Washington, DC, June 1-4, 2020

BAT287

Overview

Timeline

- Start: 10/01/2019
- Finish: 09/30/2020

Barriers addressed

- To reduce the production cost of a PHEV battery
- Na-ion and Na-metal batteries with long calendar and cycle life
- Na-ion and Na-metal batteries with superior abuse tolerance

Budget

- Funding received in FY19

  DOE: $400k

- Funding received in FY20

  DOE: $325k

Collaborators

- University of Texas-Austin
- University of Maryland at College Park
- Stony Brook University
- Oak Ridge National Laboratory (ORNL)
- Lawrence Berkeley National Laboratory (LBNL)

Relevance and Project Objectives

✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*

- Using *in situ* and *ex situ* hard x-ray absorption spectroscopy (hXAS) to study the charge compensation mechanisms of novel O3-type $NaCr_{2/3}Ti_{1/3}S_2$ and NaCrSeS cathode materials for sodium-ion batteries during charge-discharge cycling.
- Using spatially resolved 2-D x-ray fluorescence (XRF) mapping and S-K edge x-ray absorption spectroscopy (XAS, including XANES and XAFS) to study the anionic redox mechanism of $NaCr_{2/3}Ti_{1/3}S_2$ and NaCrSeS cathode materials at different SOCs.
- Using synchrotron-based *ex situ* x-ray diffraction (XRD) and Pair Distribution Function analysis (PDF) to study the structure evolution of $NaCr_{2/3}Ti_{1/3}S_2$ and NaCrSeS cathode materials during the charge/discharge processes.

✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*

- To develop *in situ* and *ex situ* diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of sodium batteries by studying the mechanism of capacity and power fading of Na-ion and Na metal batteries.

✓ *Diagnostics study of electrode materials with lower cost potential.*

BROOKHAVEN NATIONAL LABORATORY

Milestones

Month/Year	Milestones
Dec/2019	Complete spatially resolved x-ray fluorescence (XRF) image and S-K edge x-ray absorption (XAS, including XANES and EXAFS) studies of $NaTi_{1/3}Cr_{2/3}S_2$ cathode material at different SOCs. (Q1, December 2019) ➥ *Completed.*
Mar/2020	Complete synchrotron-based ex situ x-ray diffraction (XRD) and Pair Distribution Function analysis (PDF) of novel anion redox-based cathode material NaCrSeS at different SOCs. (Q2, March 2020) ➥ *Completed.*
Jun/2020	Complete the Cr and Se K-edge XAS study and analysis of NaCrSeS cathode material at different SOCs. (Q3, June 2020) ➥*On schedule.*
Sep/2020	Complete the S K-edge XANES and XAFS studies of NaCrSeS cathode material at different SOCs. (Q4, September 2020) ➥ *On schedule.*

BROOKHAVEN NATIONAL LABORATORY

Approaches

- Synchrotron based *in situ* and *ex situ* x-ray diffraction (XRD) techniques to study the phase transition and structural changes of cathode materials for Na-ion batteries during charge-discharge cycling
- Synchrotron based x-ray absorption spectroscopy (XAS), combined with spatially resolved 2-D x-ray fluorescence (XRF) mapping to study the redox mechanism of cathode materials of Na-ion batteries.
- Synchrotron based x-ray pair distribution function analysis (xPDF) to elucidate the long and short range ordering of cathode materials for Na-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

Synchrotron X-ray based techniques for sodium battery studies

23-ID-2 and 7-ID-1 @NSLS-II

18-ID and 3-ID @NSLS-II

Soft X-ray absorption spectroscopy (sXAS)

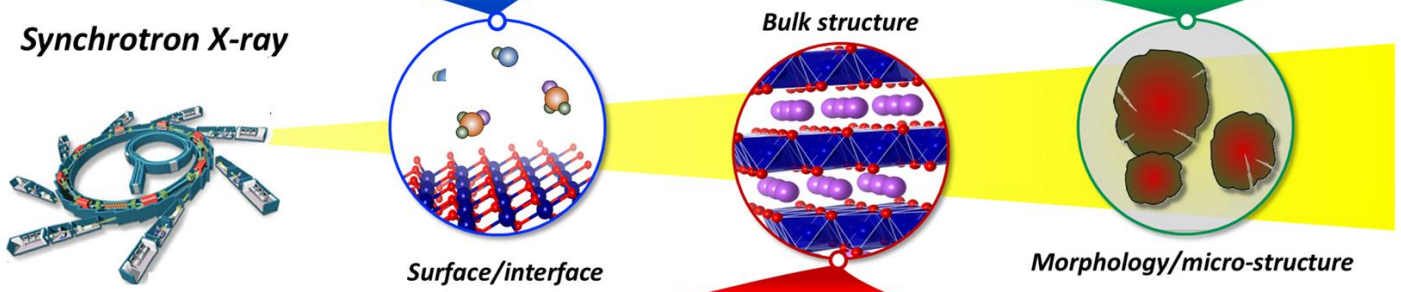
- Extremely surface sensitive
- Different modes with different probing depth
  - Auger electron yield (AEY): ~ 1nm
  - Total electron yield (TEY): ~10nm
  - Partial electron yield (PEY): ~5nm
  - Total fluorescence yield (TFY): ~ 500nm

- Requires UHV condition : limit in situ capability for liquid electrolyte

Scanning/Transmission X-ray microscopy (STXM/TXM)

- Morphology and micro-structure evaluation in micro/meso/macro scale
: Micro-crack, particle fracture, tortuosity

- Chemical information (elemental/chemical mapping)
: concentration gradient, oxidation state in single/multiple particle level (chemical inhomogeneity)



X-ray diffraction (XRD)

- Average crystal structure (long-range order)
  - Lattice parameter
  - Phase
  - Strain
  - Atomic position
  - Site occupancy
  - Texture
  - Stacking faults

Pair distribution function (PDF)

- Total scattering (Bragg+diffuse scattering)
- Local structure information
: Inter-atomic distance, coordination numbers

- Cover middle range structure between XRD and EXAFS

Hard X-ray absorption spectroscopy (XAS: XANES and EXAFS)

- Valence state changes during electrochemical reaction
: revealing charge compensation mechanism in elemental specific way
- Coordination environment (e.g., octahedral, tetrahedral etc.)
- Local structural changes
: bond length, degree of disorder

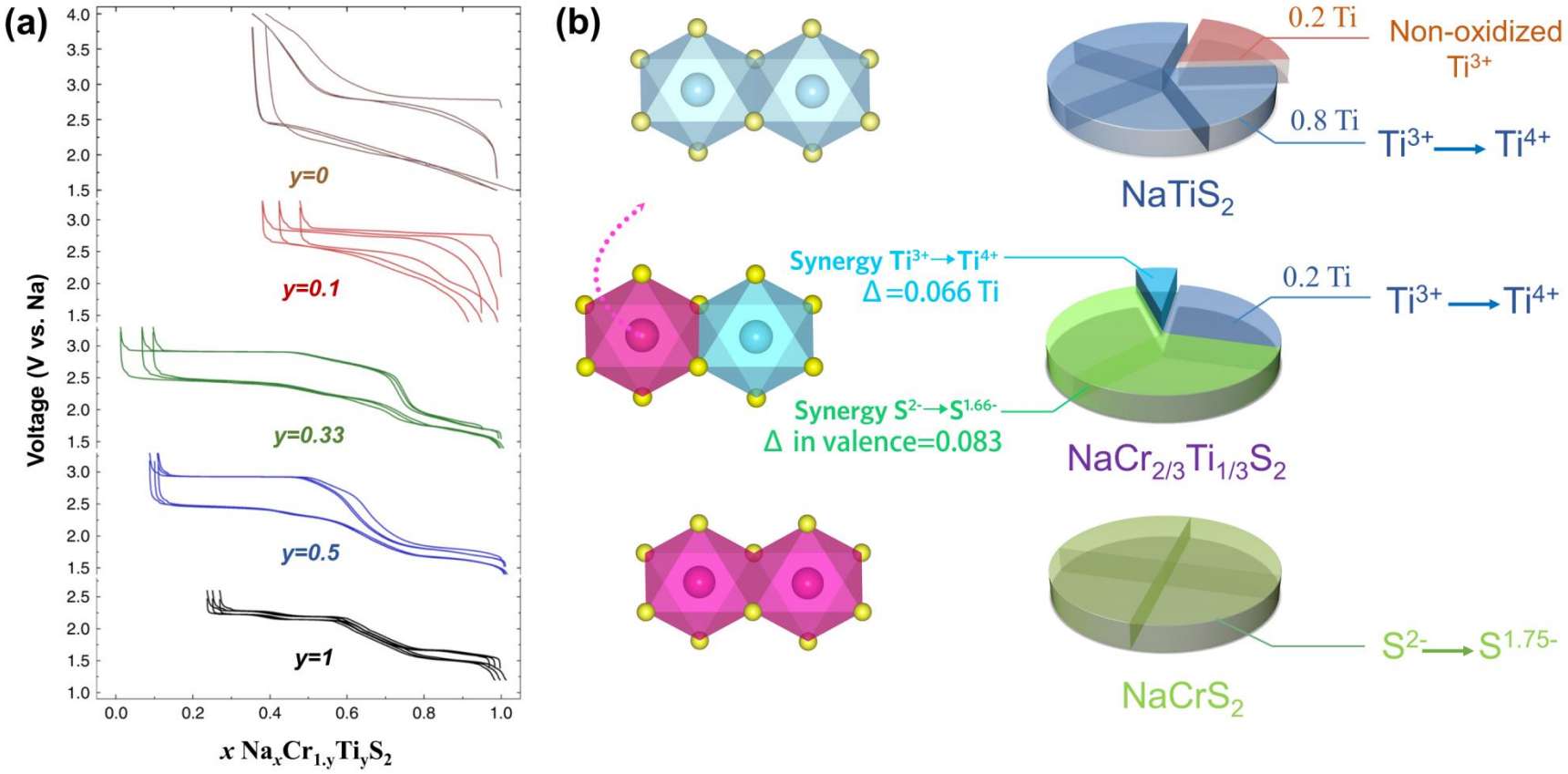
28-ID-2@NSLS-II

28-ID-1@NSLS-II

8-ID and 7-BM@NSLS-II

Technical Accomplishments

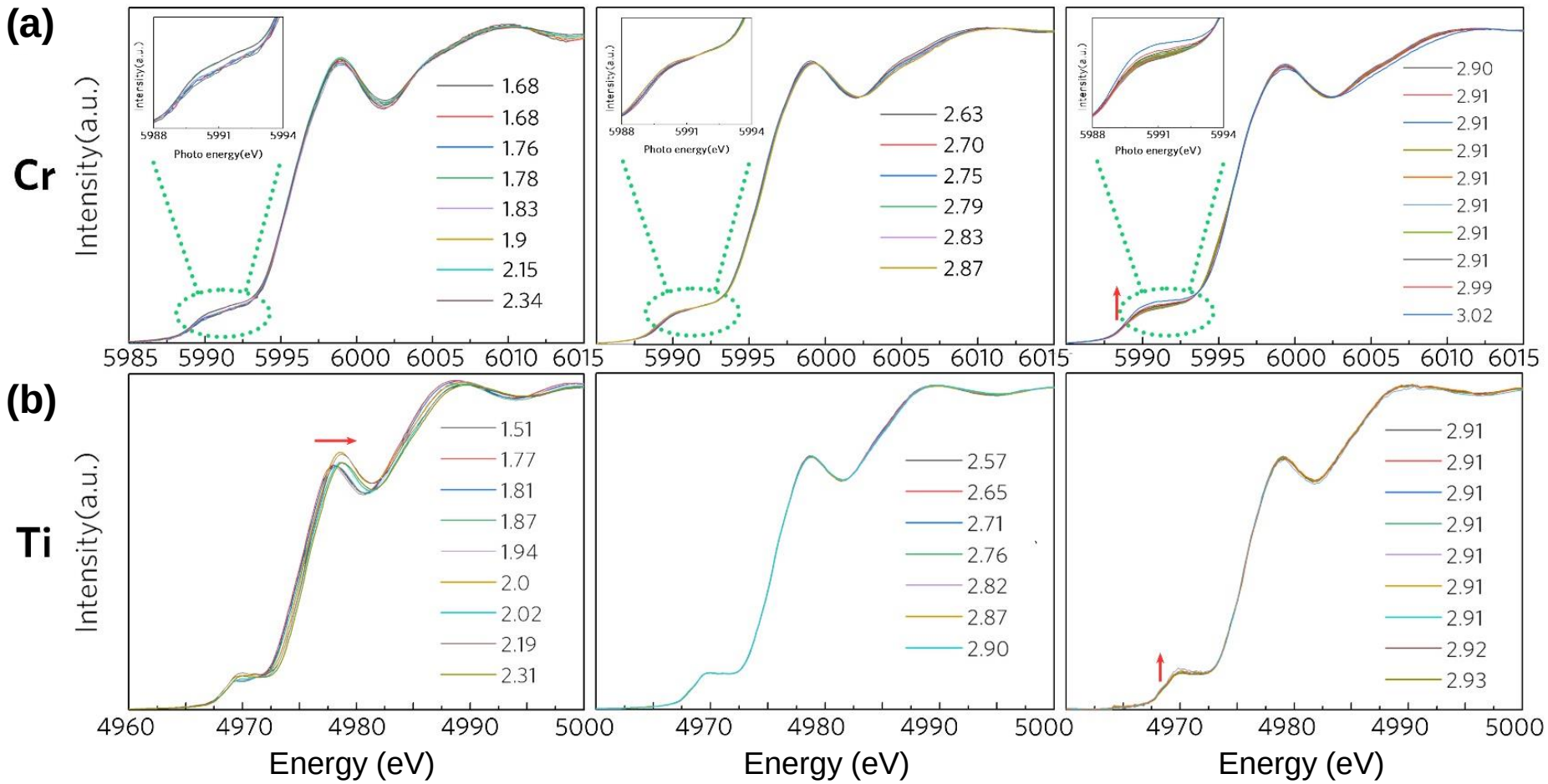
Electrochemical performance and proposed charge compensation mechanism of $NaCr_{1-y}Ti_yS_2$



- A reversible capacity of 186 mAh g^{-1} is achieved for $NaCr_{2/3}Ti_{1/3}S_2$, which is the highest value among various $NaCr_{1-y}Ti_yS_2$ cathodes.
- Such a high reversible capacity of for $NaCr_{2/3}Ti_{1/3}S_2$ is proposed to be contributed by the synergistic effect of $Ti^{3+/}Ti^{4+}$ and sulfur anion redox.

Technical Accomplishments

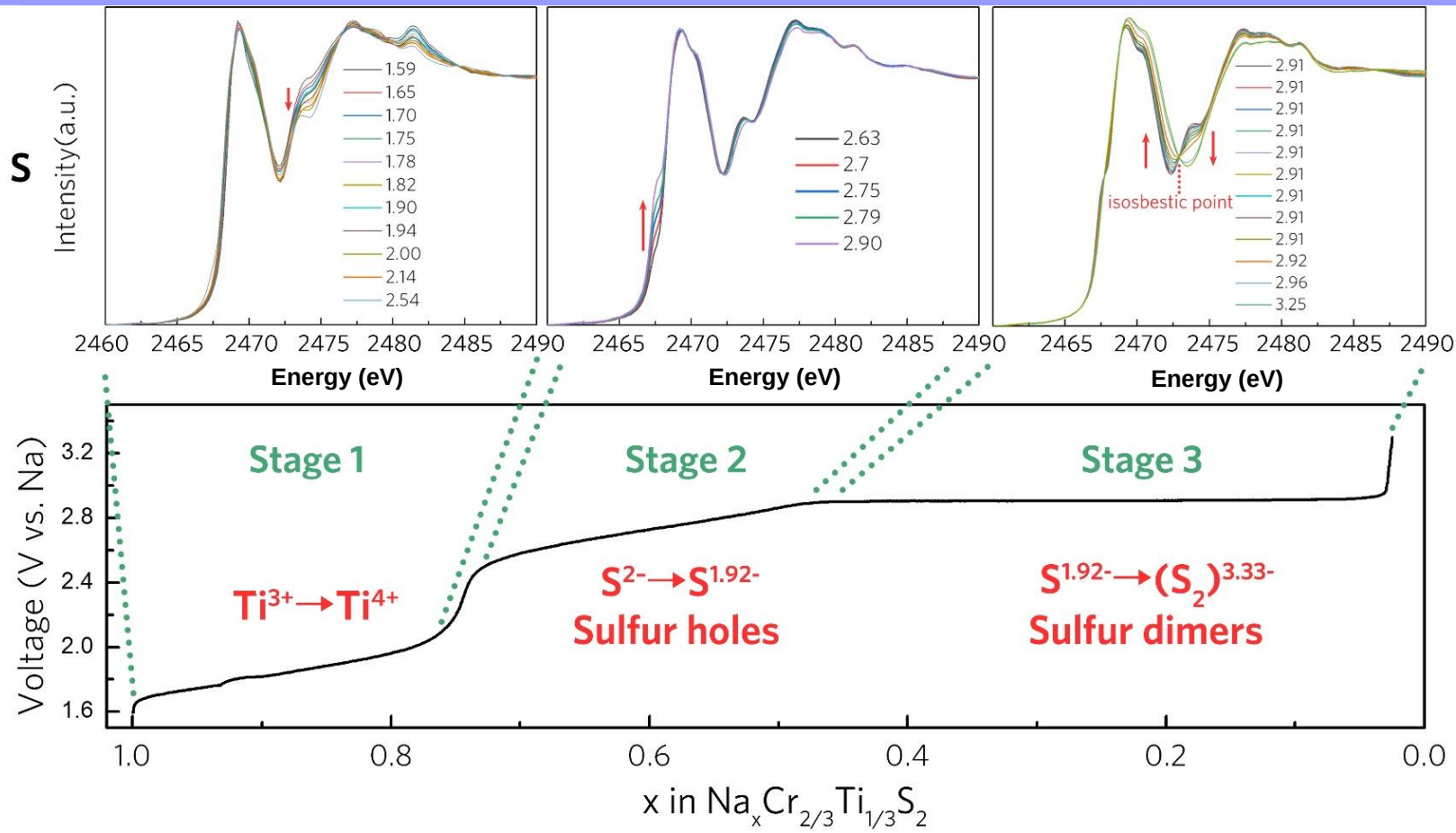
In situ Ti and Cr K-edges XAS spectra of $NaCr_{2/3}Ti_{1/3}S_2$ during the initial charging



- During the whole electrochemical process, the Cr ions do not participate in the electrochemical redox reactions. Only a small rise in pre-edge is observed.
- Ti ions oxidize at the beginning of the charging (to 2.31 V) and there is no further oxidation reaction for Ti in subsequent stages of charging (2.31-3.0 V)

Technical Accomplishments

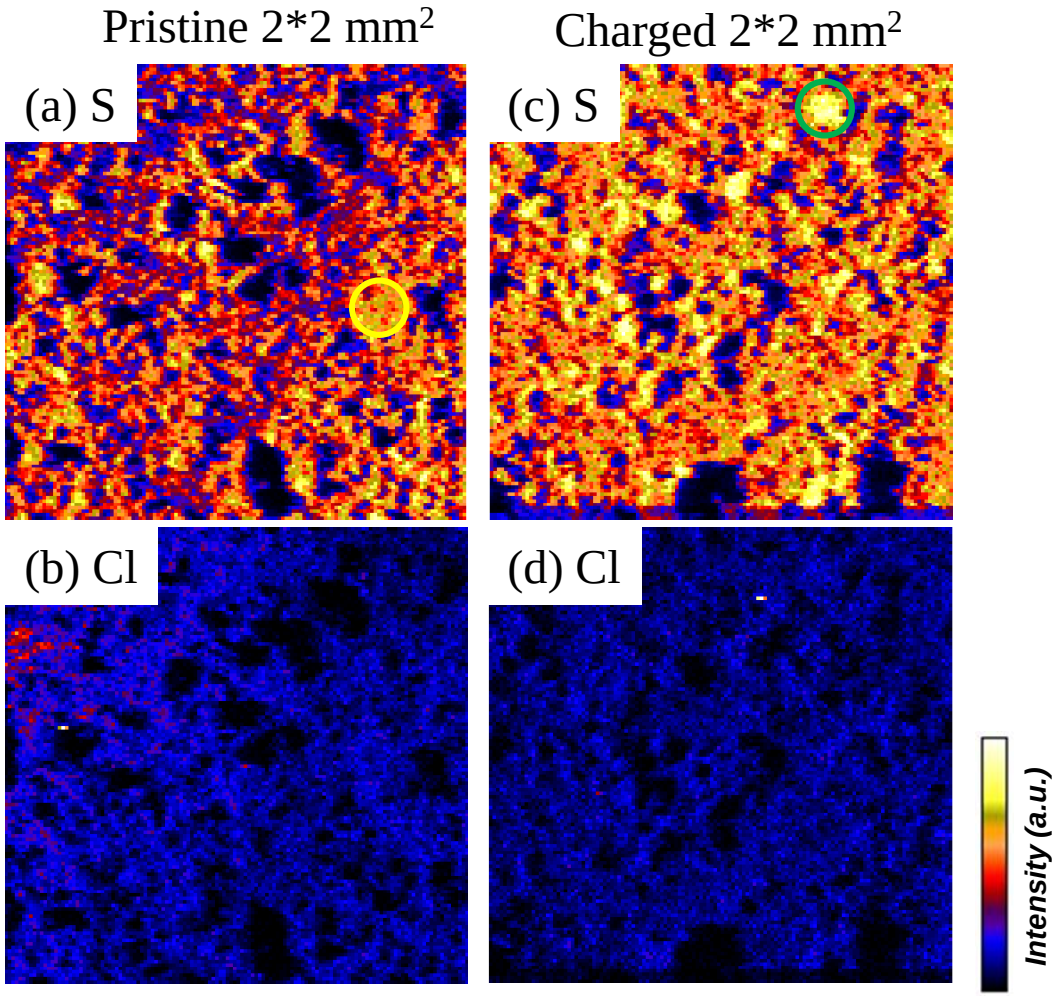
In situ S K-edges XAS spectra of $NaCr_{2/3}Ti_{1/3}S_2$ during the initial charging



- During the first stage of charging, S K-edge XAS spectra hardly changes.
- In the second stage, the shoulder peak located at ~2468 eV shows gradually increased intensity, which is attributed to the generation of electron holes on sulfur sites.
- In the third stage, a new peak appears at 2470.7 eV, which corresponds to a newly-formed localized electronic states on sulfur, probably stand for S-S σ*, resulting from the reaction of $2S^{2-}$ to $(S_2)^{n-}$ ($n < 4$).

Technical Accomplishments

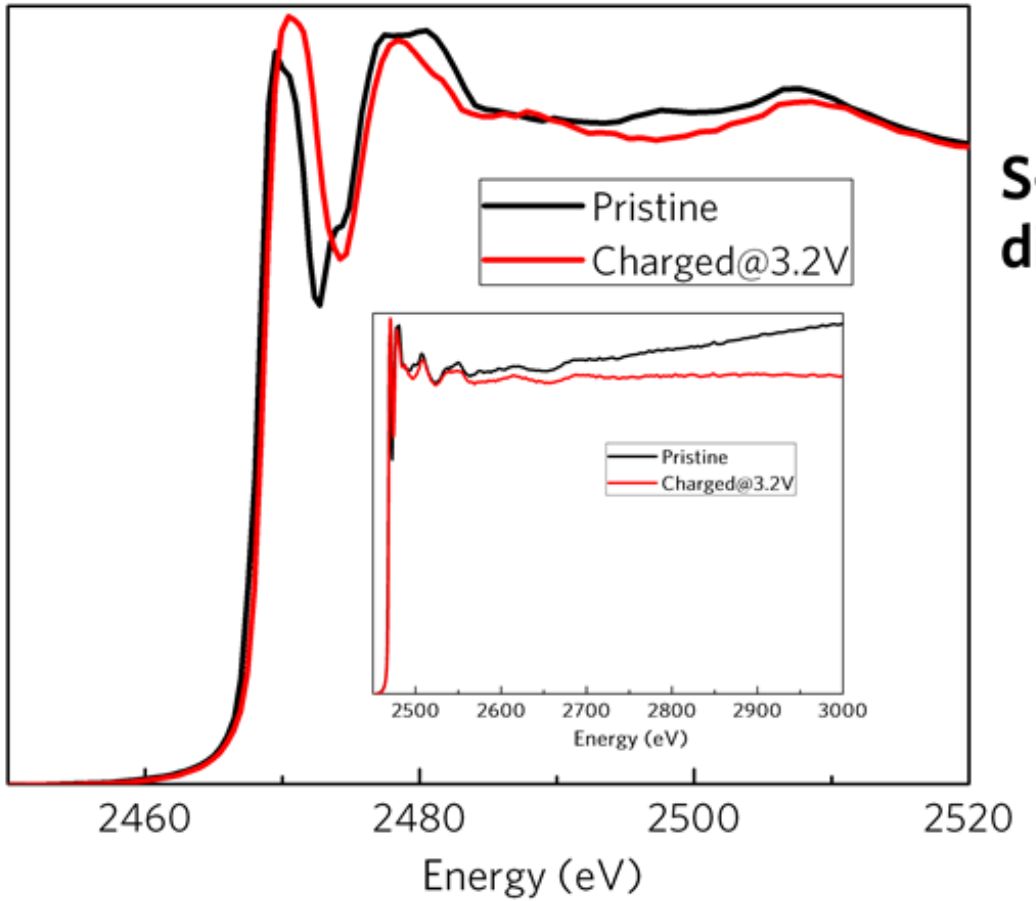
2D X-ray fluorescence (XRF) mapping of the pristine and fully charged $NaCr_{2/3}Ti_{1/3}S_2$

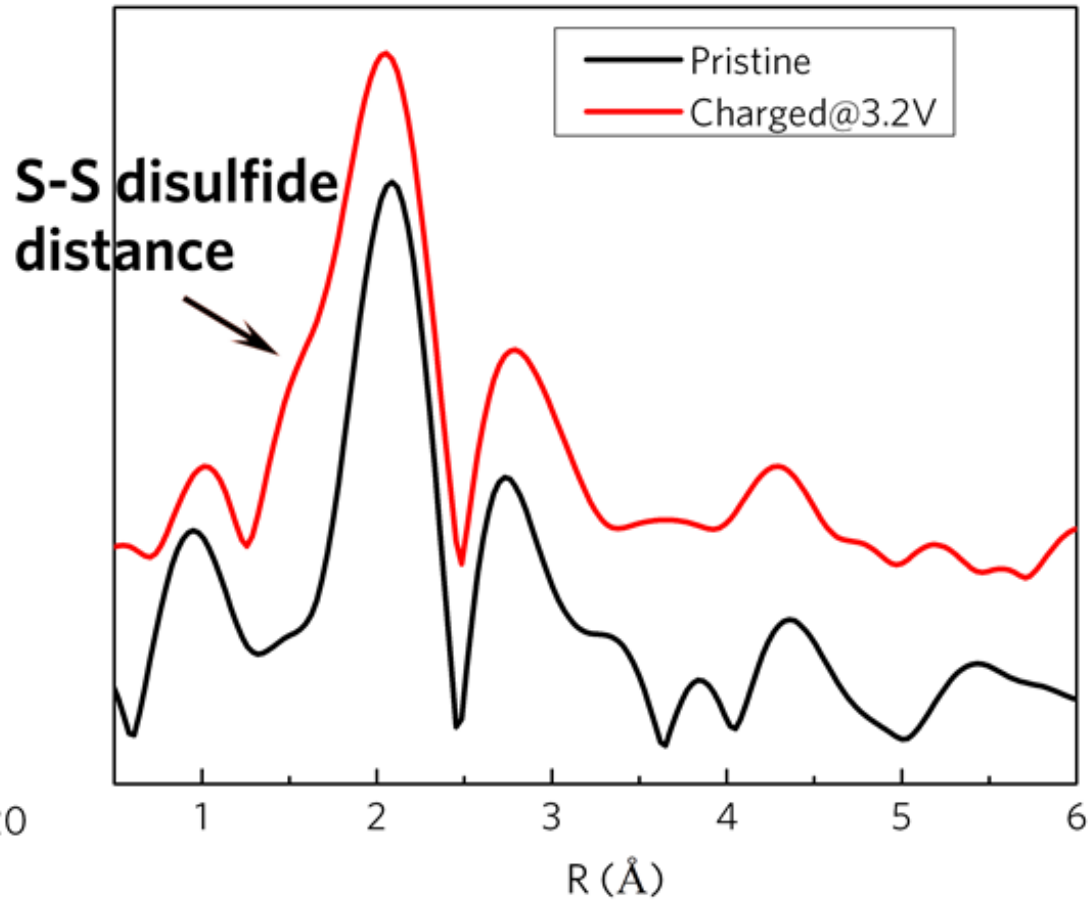


- Sulfur species is homogenously distributed in the pristine and the charged states.
- Electrode surface was covered by Cl, which is from the cathode/electrolyte interface (CEI) formed by $NaClO_4$ salt in electrolyte
- The region with high sulfur concentration and low Cl is selected for the S K-edge EXAFS measurement to avoid the interference of Cl absorption.

Technical Accomplishments

S K-edge XANES and FT-EXAFS spectrum of the pristine and charged $NaCr_{2/3}Ti_{1/3}S_2$

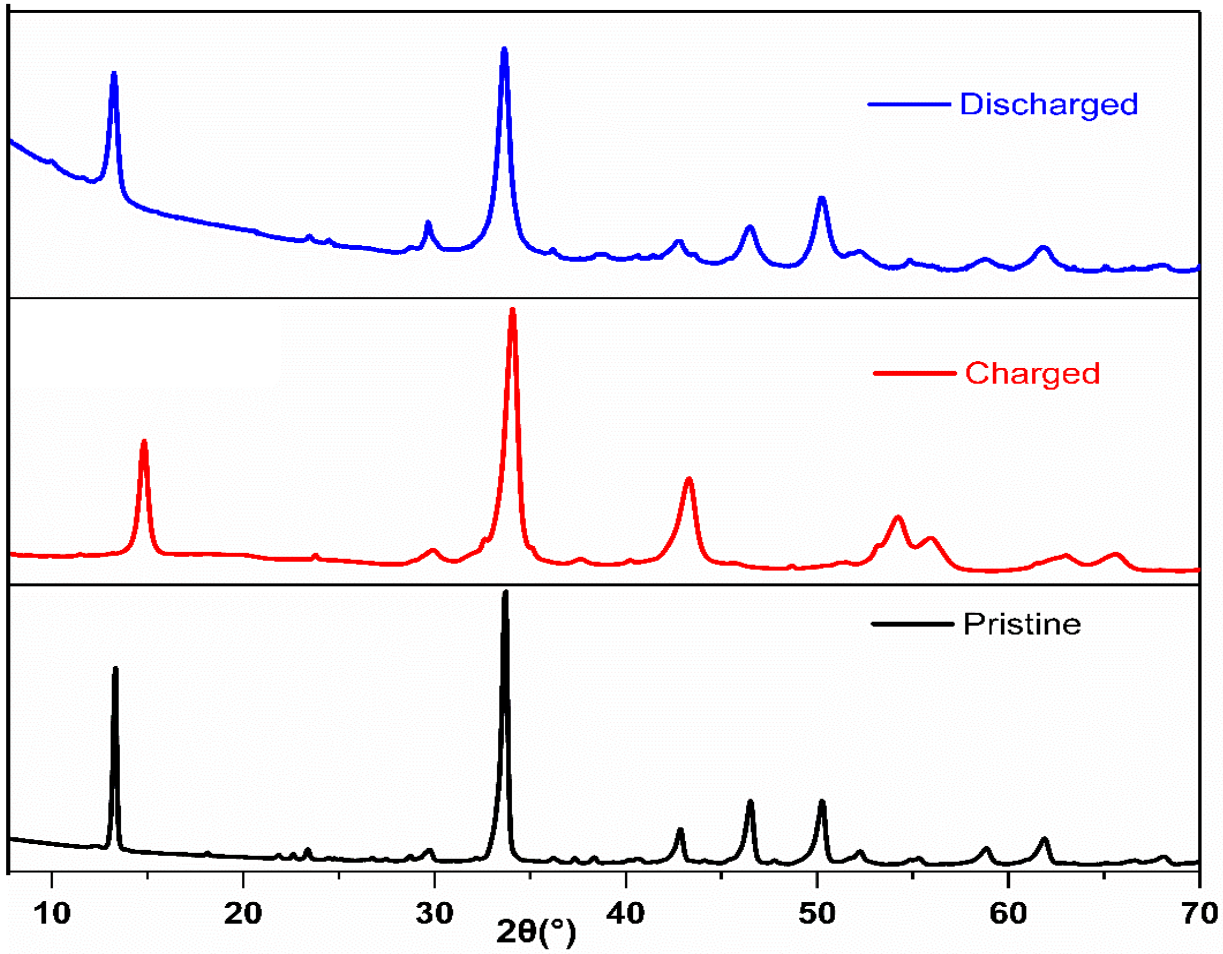




- A shoulder peak at ~1.6 Å can be observed from the FT-EXAFS spectra (right panel) of the charged sample, which is attributed to disulfide (S-S distance of 2.05 Å) formation after considering phase correction.

Technical Accomplishments

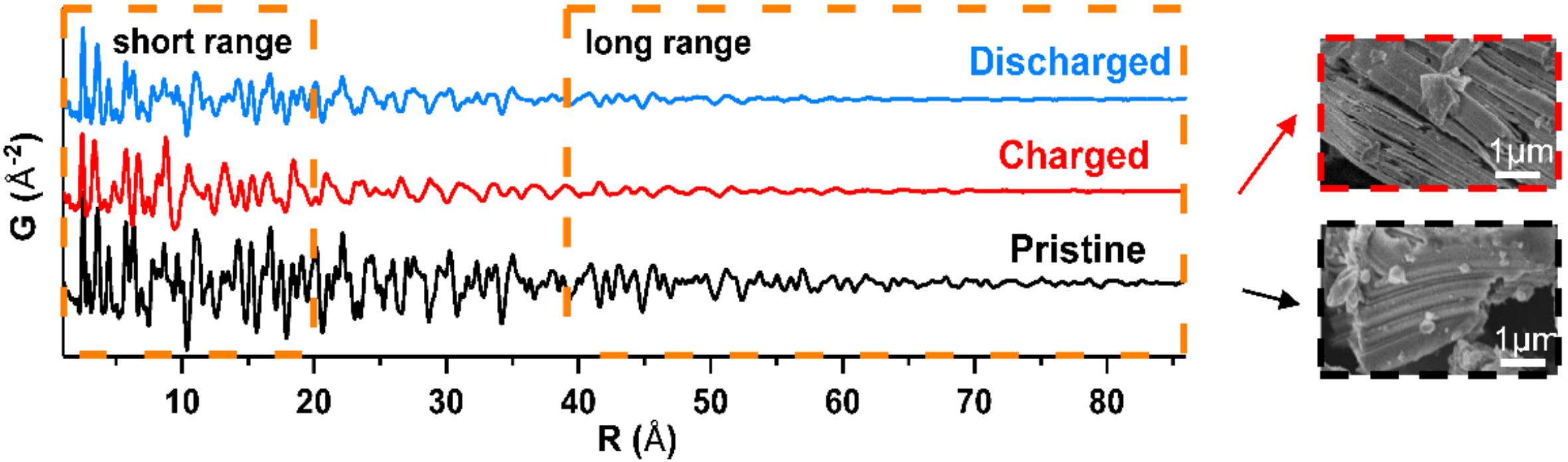
Ex aitu XRD patterns of NaCrSeS cathode material



- After charging, the characteristic peaks of O'3-NaCrSeS disappear and a new phase of O1-CrSeS forms.
- XRD pattern (2θ angles converted to corresponding to wave length of 1.54 Å)of the discharged sample fully recovers as the pristine state, indicating the good structural reversibility of NaCrSeS during the initial cycle.

Technical Accomplishments

PDF of NaCrSeS at the different SOC within the long-r range of 0-85 Å



- Within high-r range (20-80 Å), stronger G(r) peaks are observed clearly from PDF of the pristine sample even at the large atomic pair distance (60-70 Å), indicating the good crystallinity of the pristine sample.
- the intensity of G(r) peaks of charged and discharged samples reduces obviously, especially at the larger atomic pair distance (>50 Å), indicating that the charged and discharged samples have poorer crystallinity compared with the pristine sample.

Technical Accomplishments

- Through collaboration with Dr. Bohang Song, Dr. Jue Liu, and Dr. Katharine Page at Oak Ridge national Laboratory (ORNL), anionic redox mechanism of $Na_2Mn_3O_7$ cathode material using *ex situ* X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption find structure spectroscopy (EXAFS). The results of this study was published on ***Chemistry of Materials (CM)***.
- Through collaboration, charge compensation mechanism of novel O3-$NaCr_{1/4}Fe_{1/4}Ni_{1/4}Ti_{1/4}O_2$ cathode material has been studied using *ex situ* XANES and EXAFS spectroscopy, the results was published on ***Energy Storage Materials (ESM).***
- Through collaboration, charge compensation mechanism of novel O3-$NaCr_{2/3}Ti_{1/3}S_2$ cathode material has been studied using synchrotron based hard/soft XAS and 2D XRF mapping, the results were published on ***Nature Communications (NC).***
- Through collaboration, structure evolution of novel O'3-NaCrSeS cathode material has been studied using synchrotron based XRD and PDF techniques.

Response to last year reviewer's comments

Comments from 2019 AMR	Response
N/A	N/A

This project was not reviewed in 2019

Collaborations with other institutions and companies

- **Lawrence Berkeley National Laboratory**
  Sodiation Kinetics of Metal Oxide Conversion
- **University of Maryland at College Park**
  Sodiation Kinetics of Metal Oxide Conversion
- **Drexel University**
  Probing the mechanism of high capacitance sodium anode materials in 2D titanium carbides
- **University of Texas-Austin**
  Removal of interstitial H_2O in hexacyanometallates for a superior sodium battery cathode
- **Massachusetts Institute of Technology (MIT)**
  A quaternary layered cathode compound for rechargeable Na ion batteries

BROOKHAVEN NATIONAL LABORATORY

Remaining Challenges and Barriers

- N/A

Proposed Future Work for *FY 2019* and *FY2020*

▣ **FY2020 Q3 Milestone:**

Complete the Cr and Se K-edge XAS study and analysis of NaCrSeS cathode material at different SOCs.

▣ **FY2020 Q4 Milestone:**

Complete the S K-edge XANES and XAFS studies of NaCrSeS cathode material at different SOCs.

FY2021 work proposed:

- ▣ **Synchrotron based *in situ* and *ex situ* XRD and XAS techniques will be applied to study the structural stability and charge compensation mechanisms of new cathode material $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ for Na batteries.**
- ▣ **The two-dimensional (2D) XANES mapping of Mn and Ni will be applied to study the charge distribution homogeneity of new cathode material $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ for Na batteries.**
- ▣ **Synchrotron based *ex situ* XAS techniques will be applied to study the structure evolution and charge compensation mechanisms of P2-layered $Na_{0.7}Mg_{0.2}[Mn_{0.6}Fe_{0.2}\square_{0.2}]O_2$ cathode material for Na batteries (□ here representing transition metal vacancy).**
- ▣ **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

Summary

Relevance

- ✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*
- ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
- ✓ *Diagnostics study of new electrode materials with lower cost potential.*

Approaches

- *In situ and ex situ x-ray diffraction and absorption spectroscopy*
- *Synchrotron based x-ray pair distribution function (XPDF)*
- *2D X-ray fluorescence (XRF) mapping*
- *Synchrotron based transmission x-ray microscopy (TXM)*

Technical Accomplishments

- *Anionic redox mechanism of $Na_2Mn_3O_7$ cathode material has been studied using ex situ XANES and EXAFS.*
- *Charge compensation mechanism of novel O3-$NaCr_{1/4}Fe_{1/4}Ni_{1/4}Ti_{1/4}O_2$ cathode material has been studied using ex situ XANES and EXAFS spectroscopy.*
- *Charge compensation mechanism of novel cathode material O3-$NaCr_{2/3}Ti_{1/3}S_2$ has been studied using in situ XAS spectra and 2D XRF mapping.*
- *Structure evolution of novel cathode material O'3-NaCrSeS has been studied using ex situ XRD and PDF techniques.*

Proposed Future work

- *Continue and complete the charge compensation mechanism study of O'3-NaCrSeS by ex situ XAS spectroscopy.*
- *Synchrotron based XRD and XAS, as well as TXM techniques will be applied to study the charge/discharge mechanisms of new cathode material s $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ and $Na_{0.7}Mg_{0.2}[Mn_{0.6}Fe_{0.2}\square_{0.2}]O_2$ for sodium batteries.*
- *Develop and apply the neutron diffraction (ND) and neutron PDF techniques for sodium battery material studies*